Comparison of two different HCHO Measurement Techniques: TDLAS and a commercial Hantzsch Monitor – Results from Long-term Measurements in a City Plume during the EVA Experiment.

A contribution to EUROTRAC subproject GENEMIS, Annual Report 2001

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Objectives

For the evaluation of an emission model two field campaigns have been performed in the Augsburg area in March and in October 1998. As part of an integrated concept (Slemr et al., 2002) of ground-based and air-borne measurements as well as tracer experiments the long-term measurements were applied to characterize the composition of the city plume of Augsburg. For this purpose a mobile laboratory was placed 5 km downwind of Augsburg in Stätzling, equipped with analytical instruments for the measurement of NO, NO_2, NO_y, CO, $C_2 - C_{10}$-hydrocarbons, HCHO, O_3 and meteorological parameters.

Activities

The results of our evaluation of the utilized emission model (Kühlwein et al.) by ground-based measurements with respect to CO-, $C_2 - C_{10}$-hydrocarbon- and NO_x-emissions have already been reported in the last annual report (Klemp et al., 2001) and will be published in a special issue of Atmospheric Environment (Klemp et al., 2002, Mannschreck et al., 2002).
In this paper special emphasis is placed on the results of atmospheric HCHO concentrations, measured by two different measurement techniques: Tunable Diode Laser Absorption Spectroscopy (TDLAS) and a commercial Hantzsch monitor. The following methodical approach is used for the determination of emission ratios Augsburg from concentration measurements:

- Contamination from local sources is eliminated by both the choice of an appropriate measurement size and by careful data screening.
- The data were grouped into 10-minutes averages and were filtered by wind direction as well as by wind speed (10-minutes averages with wind speeds < 3 m/s are rejected) in order to exclude the city sector from the data as well as to minimize the influence of photochemical processes.
- In order to exclude substantial degradation or production of the species by means of photochemical processes during transport from the city to the receptor place, the measurements are performed out of the summer period. Concurrently measured NO_y/NO_x ratios are around 1.1, which points out that photochemical processes during transport are neglectible.
- Only ratios of data rather than absolute concentrations are considered. These are determined by correlation analyses. Thus, the background levels (i. e. levels upwind of the city) of the respective trace gases as well as meteorological influences are eliminated.
- The spacial representativity of the long-term data set is ensured from the comparison of the Stätzling data with the results of air-borne measurements, which show consistent results (Klemp et al., 2002).

Experimental

Formaldedyde and NO, NO_2 and NO_y were continuously measured over a period of more than 4 weeks at Stätzling in the north-east of Augsburg in March 1998. Analytical instruments for the measurement of HCHO, NO_x and NO_y are part of the equipment, which is installed in the air conditioned mobile laboratory of Forschungszentrum Jülich (FZJ) (Klemp et al., 2002). The inlets were mounted on a pneumatic mast 10 m above the surface. For all connections PFA tubing (¼ inch OD) were used.

Formaldehyde: The commercial *Hantzsch monitor* detects HCHO by fluorescence of 3,5-diacetyl-1,4-dihydrolutidin (Dasgupta et al., 1988), which is produced from the reaction of HCHO with 2,4-pentadione and NH_3. Atmospheric HCHO is transferred quantitatively into the liquid phase using a stripping coil, which was kept at a constant temperature of 15 °C. Zero signals were determined by scrubbing HCHO from ambient air using a Hopcalite® filter. The instrument was calibrated by a relative and an absolute procedure. Relative calibrations were performed daily using the internal HCHO permeation device. Absolute calibrations were made once a week using a series of liquid standards ($2 * 10^{-8} – 2 * 10^{-7}$ M). With respect to the 10 minutes intervals an average detection limit of 100 ppt (2-σ) and a precision of 10 % at ambient air levels above 1 ppb were achieved during the EVA campaign.

The *TDLAS technique* is based on the monitoring of the specific absorption from a single rotational-vibrational line in the middle infrared spectrum of the molecule of interest. In order to achieve detection limits which allow to monitor atmospheric concentrations of HCHO a White cell (total light path ≈ 100 m) at reduced pressure (30 hPa) is used. Due to the reduced pressure the probability of overlap between absorption lines from other atmospheric species is nearly excluded by reducing the pressure broadening of the rotational lines. In combination with 2-f-derivative detection technique (modulation frequency: 12.5 kHz) optical densities of less than 10^{-5} can be measured. The time resolution of this technique is only limited by the exchange time (< 10 s) of the ambient air, which is pumped at the reduced pressure through the White cell. In order to monitor slowly variating background structures, which limits the attainable detection limit of the TDLAS, background spectra were monitored every 5 – 10 minutes by adding N_2 instead of ambient air at the inlet system. Calibrations were performed every 30 minutes by adding a known mass flow of HCHO from a home-built thermostated permeation device to a N_2 gas stream at the inlet. Ambient air concentrations were calculated from the comparison of the ambient air spectrum with that from the respective calibration cycle by means of a non-linear fit procedure. The HCHO mass flow of the permeation device was absolutely calibrated by two independent methods: gravimetrically and colorimetrically as described in (Harris et al., 1989). For the TDLAS technique a detection limit of 200 ppt (2-σ, 10-minutes averages) is achieved throughout the EVA campaign and the precision of the TDLAS measurements at more than 2 ppb is calculated to be 10 %.

NO_x and NO_y were measured using two chemiluminescence detectors (ECO Physics, CLD 770AL ppt), a photolytic converter (ECO Physics PLC 760) to convert NO_2 to NO, and a home-built gold converter to convert NO_y (i.e. $NO_x = NO + NO_2$ and its oxidation products, mainly HNO_3) to NO on a hot gold surface (Fahey et al., 1986), which was directly placed on top of our pneumatic mast in order to avoid NO_y losses. NO calibrations were performed daily by adding a known flow of calibration gas (10 ppm NO in N_2) into the NO_x-free air stream. The conversion efficiencies of the PLC and the Au-converter for NO_2 were also determined every night. The conversion efficiency of the Au-converter for HNO_3 was checked weekly using a home-built permeation source. For NO a precision of 8 % and a detection limit of 20 ppt (2-σ) were achieved for an integration time of 10 minutes. The corresponding data for NO_2 and NO_y are 9 % and 30 ppt, and 8 % and 200 ppt, respectively.

Results

a) Mean HCHO/NO_x-ratios

Figure 1 shows mean formaldehyde concentrations of the EVA-1 campaign (based upon 10-minutes averages, measured by a TDLAS system) as a function of NO_x concentrations. 10-minutes averages of HCHO were grouped by different classes of NO_x (ΔNO_x = 2ppb) and mean formaldehyde concentrations, 25-and 75-percentiles were calculated for each individual NO_x-class. The error bars indicate that the scatter of measured ratios of HCHO/NO_x (10-minutes averages) is of the same order of magnitude as the observed HCHO signal of the city. It is well known that as a moderately water soluble species HCHO is efficiently washed out by precipitation (effective Henry´s law coefficient including diol formation: 6300 M atm^{-1} (Seinfeld and Pandis, 1998)). Grouping of HCHO concentrations by classes of a co-emitted and in the first approximation non-soluble NO_x and further averaging will separate the meteorological influence from the emissions of Augsburg. Using this approach it is assumed that the mean HCHO concentrations calculated for the different NO_x-classes consists of a mean HCHO background concentration and a NO_x-dependent HCHO term, which describes the HCHO/NO_x emission ratio of Augsburg. This assumption is reasonable, because wash-out of HCHO would influence the HCHO background concentrations rather than cause losses during less than 30 min long transport between Augsburg and the Stätzling site. In fact, the averaged formaldehyde concentrations correlate positively with NO_x concentrations (R^2 = 0.88).
Figure 1 suggest two conclusions: i) The regression of HCHO with NO_x yields a HCHO/NO_x emission ratio of around $(3.7 \pm 0.5) \cdot 10^{-2}$ ppb/ppb for fresh emissions. ii) The extrapolation of formaldehyde to the seasonal NO_x background concentration of 1 ppb (Mannschreck, 2001) yields a background concentration of HCHO of (0.6 ± 0.1) ppb.

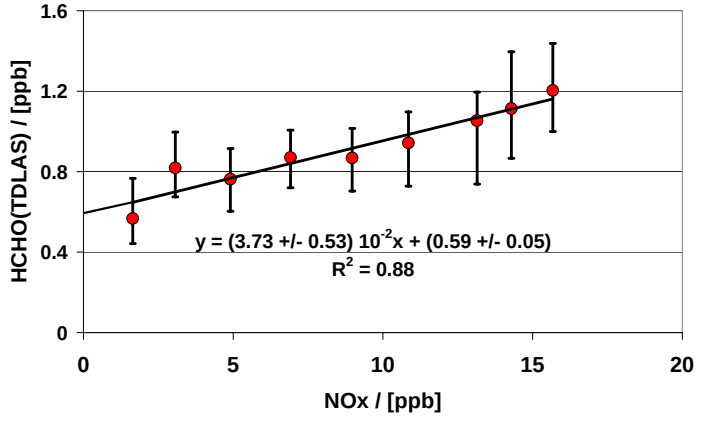

Fig. 1: Mean formaldehyde concentrations (based upon 10 minutes averages, March campaign) for different NO_x-classes (ΔNO_x = 2 ppb). The error bars indicate the 25-and 75-percentiles of formaldehyde for each NO_x-class. HCHO measurements were carried out by a home-built Tunable Diode Laser Absorption Spectrometer (TDLAS). The mean slope and its 1-σ-standard deviation as well as R^2 are calculated by orthonormal regression analysis.

The same type of investigation is performed for the HCHO mixing ratios measured by the Hantzsch monitor during the EVA-1 campaign. Table 1 shows that both the HCHO/NO_x ratios and the HCHO background concentrations are in good agreement for the two independent measurement techniques.
Also listed in Table 1 is the mean emission ratio of HCHO/NO_x = $3.3 \cdot 10^{-2}$ ppb/ppb for March 1998 from the emission model provided by IER Stuttgart (Kühlwein et al. 2002). Within their error limits, experimentally derived HCHO/NO_x-ratios agree with those from the emission model.

Table 1: Comparison of experimentally derived HCHO/NO_x ratios with those from the emission model, provided by IER, Stuttgart (Kühlwein et al., 2002) for the March campaign. In case of the experimental results HCHO values were clustered by NO_x intervals of ΔNO_x = 2 ppb and correlation analyses were performed. Two different HCHO measurement methods were used (a commercial Hantzsch system (AL4) and a TDLAS system (TDL)).

	HCHO/NO_x (ppb/ppb)	HCHO-Background (NO_x=1 ppb) (ppb)
AL4	$(3.28 \pm 0.48) \cdot 10^{-2}$ R^2 =0.82	0.49 ±0.07
TDL	$(3.73 \pm 0.53) \cdot 10^{-2}$ R^2 =0.88	0.61 ±0.05
Emission model	$3.3 \cdot 10^{-2}$	- -

b) Comparison of concurrently measured HCHO concentrations

In Fig. 2 more than 1000 concurrently measured 10-min averages are plotted. Only data from the city sector are considered. In order to study the effect of longer transport times from the city to the receptor place, the wind speed limit is set to 0.5 m/s. For most pairs of measurements (i. e. HCHO < 2 ppb) both detection techniques yield comparable mixing ratios. For higher mixing ratios, however, some Hantzsch measurements exceed those of TDLAS by up to a factor of two.

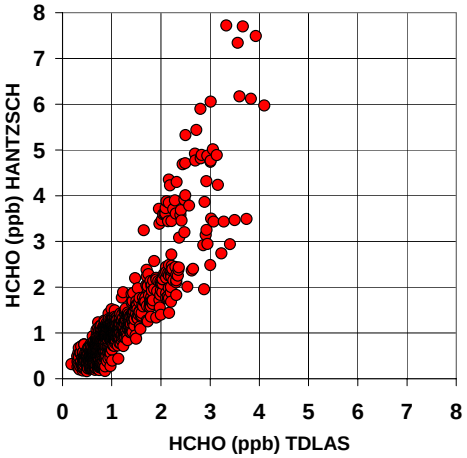

Fig. 2: Result of concurrently measured HCHO concentrations (Hantzsch monitor and TDLAS, 10 minutes averages) during the EVA campaign (2. 3. – 31. 3. 1998) downwind of Augsburg.

As shown in Fig. 3, both subsets of data can be successfully separated using the concurrently measured NO_x concentrations and the respective NO_y/NO_x-ratios as filter criteria. The NO_y/NO_x-ratio is used as a "photochemical clock" in order to calculate the effect of photochemistry on the measured air masses which are transported from Augsburg to the receptor site. Changes in the NO_y/NO_x-ratio of an air mass are mainly caused via OH attack of NO_2 to produce (water soluble) HNO_3. In the absence of precipitation events the NO_y/NO_x-ratio of an air mass is a measure for its photochemical exposure. That means, for freshly polluted air masses the respective NO_y/NO_x-ratio is close to 1. A quite good agreement between TDLAS and Hantzsch in the Augsburg plume is observed in fresh emissions ($NO_y/NO_x < 1.25$) and for low and moderately polluted conditions ($NO_y^{Mean(EVA-1)}$ = 8.36 ppb). The orthonormal regression analysis yields a slope of $HCHO^{HANTZSCH}/HCHO^{TDLAS}$ = 1.05 (R^2 = 0.83). During heavily polluted events (NO_y > 20 ppb) and for photochemically active conditions ($NO_y/NO_x > 1.25$) the slope is $HCHO^{HANTZSCH}/HCHO^{TDLAS}$ = 1.81 (R^2 = 0.71).

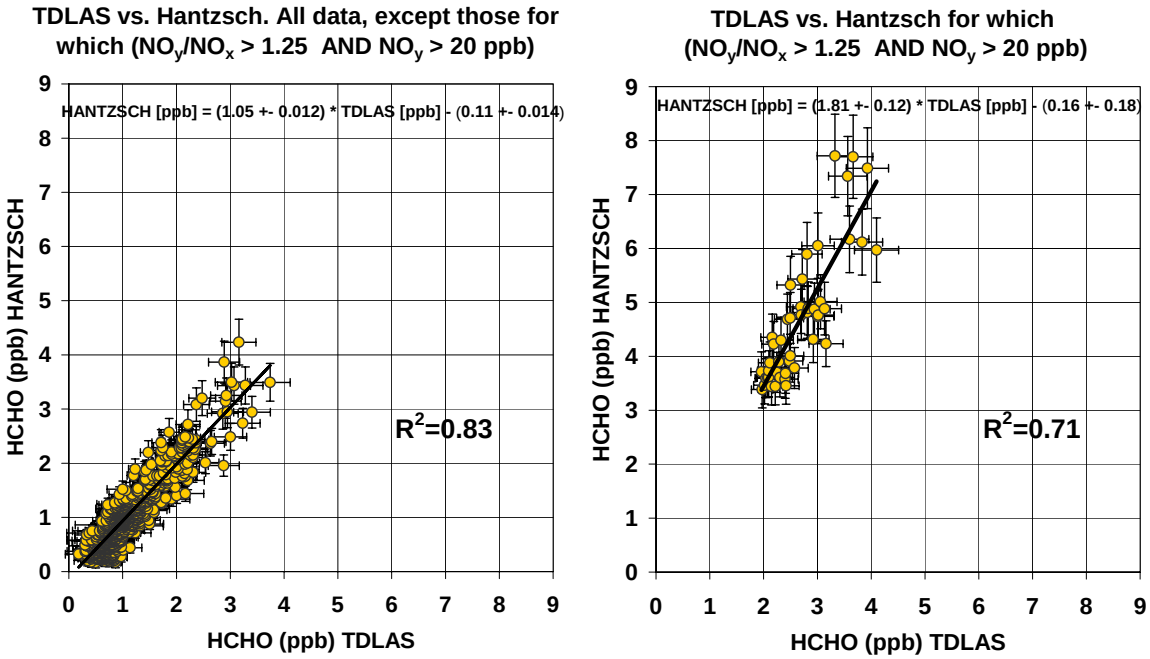

Fig. 3: Result of correlation analysis (orthonormal regression) between Hantzsch and TDLAS using (NO_y/NO_x > 1.25 and NO_y > 20 ppb) as separation criteria. The error bars denote the respective 2-σ errors of the individual 10-minutes averages.

If photochemically active conditions connected with high precursor concentrations are excluded from the long-term data set the HCHO measurements of Augsburg yield an agreement within 5 % between Hantzsch and TDLAS. Moreover, from the good accordance between both methods outside photochemically active conditions and from the stability of calibration signals, calibration errors can be excluded to be the reason for the observed deviations.

In principle, with respect to the observed deviations between both HCHO measurement techniques during photochemically active periods two explanations are possible: a positive interference of the Hantzsch technique caused by unknown species or a negative interference, which reduces the TDLAS absorption signal.

The latter explanation seems to be rather unlikely. Any interference by an additional species at the same spectral range would even enhance the measured absorption signal of the TDLAS system and could not explain HCHO mixing ratios which are up to a factor of two smaller than those measured by Hantzsch. Saturation effects of the TDLAS system, which may decrease the sensitivity of the system can also be excluded: An excellent linearity (R^2 > 0.99) of the TDLAS system is observed between 0 and 15 ppb (Klemp et al 1994).

Conclusions

The comparison between measured and calculated (Kühlwein et al. 2002) $HCHO/NO_x$ ratios for March 1998 yield an excellent agreement. Within their error limits, experimentally derived $HCHO/NO_x$-ratios agree with those from the emission model.

A quite good agreement within 5 % between two different HCHO measurement techniques (Hantzsch and TDLAS) is observed in the course of long-term emission measurements, if photochemically active conditions are excluded from the data.

For heavily polluted events with ongoing photochemistry the Hantzsch system shows higher values of up to a factor of two and the deviations between concurrently measured HCHO values yield up to 4 ppb. We did not find any indication for interferences of the TDLAS system. Moreover, interferences of the TDLAS system are rather unlikely since due to its highly selective spectroscopic detection principle TDLAS often acts as reference system against which other methods are often compared. So, we suggest that the Hantzsch HCHO levels are biased by interferences under those conditions. On the other hand, the reasons for this behaviour are still unknown and point out the need of further HCHO intercomparisons at ambient air levels, which should also include other spectroscopic techniques.

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